

REMARKS

Claims 1-5, 12 and 14-16 are pending in this application, of which claims 1, 6, 12, 17 and 21 being independent. Claims 6-11 and 17-21 have been withdrawn.

Applicant notes that US2006/0115408 cited in the present Office Action is not listed in Form PTO-892 attached to the previous Office Action dated November 26, 2008. It is respectfully requested that the Examiner provide a Form PTO-892 which properly lists US2006/0115408 in the next official communication.

Claim Rejection – 35 U.S.C. § 103

Claims 1-3 and 12 were rejected under 35 U.S.C. § 103(a) as being unpatentable over WO 03/086971 (“Starchenko”) and further in view of U.S. Patent Publication Number 2005/0110024 (“Swain”). Claim 4 and 5 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Starchenko in view of Swain as applied to claim 1, and further in view of WO 2004/046062 (“Akaishi”). Claims 12-14 were rejected under 35 U.S.C. § 103(a) as being unpatentable over JP 2001-021521 (“Meidensha”) and further in view of Swain and further in view of Starchenko. Claims 15 and 16 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Meidensha, Starchenko and Swain as applied to claims 12 and 2 above, and further in view of Akaishi. Applicant respectfully traverses these rejections for at least the following reasons.

Applicant respectfully notes that one of the features of the present subject matter is that the high-hardness conductive diamond polycrystalline body is obtained by directly converting a graphite-type carbon material including boron into diamond and concurrently sintering at high temperature and high pressure, so that the boron is included in a lattice site of the particle of the

diamond. As a result, boron is included in the diamond as substitution solid solution and the diamond polycrystalline body of the present disclosure is that of single-phase diamond.

Turning to the cited references, Starchenko discloses that diamond powder and graphite or hBN are mixed. Graphite and hBN merely function as solidification material. Accordingly, the diamond material of Starchenko essentially consists of plural phases. Swain and Meidensha disclose the diamond polycrystalline body obtained by a CVD method. Applicant respectfully submits that these prior art references are different from the claimed subject matter for at least the following reasons.

In Starchenko, boron is not included in the diamond crystal as substitutional solid solution because graphite and hBN merely function as solidification material. In addition, Starchenko does not disclose the diamond material consists of single-phase diamond. Thus, the property of the diamond polycrystalline body of the present disclosure is essentially different from that of the diamond material of Starchenko.

Regarding Swain and Meidensha, since the diamond polycrystalline bodies of Swain and Meidensha are not sintered, hydrogen impurities and SP^2 carbon as graphite bond are easily left at the grain boundary. As shown in Fig. 4 of Swain, peaks at 1470cm^{-1} and 1550cm^{-1} are observed, which indicates existence of SP^2 bonds (i.e., graphite phase). Further, Applicant submits that the attached materials (2) and (3) exhibit that the diamond of Swain and Meidensha include SP^2 bonds (i.e., graphite phase). The material (2) (Chinese Science Bulletin Vol. 48 No. 23 December 2003) shows Raman spectra of MOCVD diamond film in Fig. 2. The material (3) (Physical Review B, VOLUME 63 121405(R)) shows Raman spectra of CVD nanodiamond in Fig. 2. As shown in these figures, both SP^2 signal and SP^3 signal are observed in general CVD diamond. In the materials (2) and (3), the intensity of SP^2 signal is higher than that of SP^3 signal.

As such, it is clear that the CVD diamonds of Swain and Meidensha are not single-phase diamonds but include a graphite phase.

In contrast, in the present disclosure, peaks at 1470cm^{-1} and 1550cm^{-1} are not observed as shown in the attached material (1). The material (1) indicates Raman-spectrum chart of the sintered body of the present disclosure measured using excitation light of 523nm. By Raman spectroscopy, the information regarding the bonding state of atoms consisting of the crystal body is obtained. When the SP^3 bonds exist, a peak around 1333 cm^{-1} is observed. As shown in the attached material (1), the peak around 1333 cm^{-1} is clearly observed, but no peak corresponding to SP^2 bonds is observed. In view of the above, all of the bonds between the carbon atoms in the diamond crystal of the present disclosure are entirely SP^3 bonds.

Further, in the diamonds of Swain and Meidensha, hardness of the diamond polycrystalline bodies is reduced since the hydrogen impurities and the SP^2 carbon are left at the grain boundary and it is difficult to obtain a high-hardness diamond polycrystalline body by Swain and Meidensha. In contrast, according to the present disclosure, a high-hardness diamond polycrystalline body is obtained because all of the bonds between the carbon atoms in the diamond crystal are entirely SP^3 bonds and the impurities do not exist at the boundary.

As such, it is clear that the property of the diamond polycrystalline body of the present disclosure is clearly different from that of the diamond polycrystalline bodies of Swain or Meidensha.

Furthermore, Applicant submits that contrary to the Examiner's assertion that Starchenko discloses that graphite can be subjected to a high pressure as well as temperature, Starchenko discloses that the diamond is produced at low temperature and a low pressure (see, Abstract). Thus, the Examiner's assertion has no merit and it is clear that Stachenko fails to disclose that

“said high-hardness conductive diamond polycrystalline body is obtained by directly converting a graphite-type carbon material including boron into diamond and concurrently sintering at high temperature and high pressure,” as recited by claims 1 and 12.

Applicant further submits that Meidensha fails to disclose at least 1,000 ppm and at most 100,000 ppm of boron in the diamond body, as recited by claim 12. **Applicant submits that the boron concentration of 10^4 ppm in Meidensha is the concentration of B with respect to C (B/C) in the mixture of B_2O_3 and acetone and methanol, i.e. the source material (see, paragraph [0025] of Meidensha), but is not the concentration of boron in the diamond particle.** Paragraph [0025] of Meidensha states (machine translation from the JPO website):

[0025]As a film deposition system, using the microwave CVD-film-formation device made from ASTeX, the conductive diamond electrode in this embodiment was produced with the microwave plasma assistant CVD method, as shown below. First, after carrying out texturing treatment (it grinds with 0.5 micrometer of diamond powder) of the silicon substrate surface, using a silicon substrate (Si (100)) as said conductive substrate, said silicon substrate was fixed to the electrode holder of a film deposition system. What dissolved the quantity which serves as **10^4 ppm by boron / carbon (B/C) ratio in boron oxide (B_2O_3) in the mixture** was used, using the mixture (fluid; mixture ratio, a volume ratio 9:1) of acetone and methanol as sauce for membrane formation (emphasis added).

Applicant submits that since the Examiner failed to provide any technical reasoning why this paragraph discloses the *boron concentration in the diamond particle*, the Examiner failed to meet his burden to establish prima facie obviousness.

Based on the foregoing, Applicant respectfully submits that claims 1 and 12 and all claims dependent thereon are patentable over the cited references. Thus, it is requested that the Examiner withdraw the rejections of claims 1-5 and 12-16 under 35 U.S.C. § 103(a).

CONCLUSION

Having fully responded to all matters raised in the Office Action, Applicant submits that all claims are in condition for allowance, an indication for which is respectfully solicited. If there are any outstanding issues that might be resolved by an interview or an Examiner's amendment, the Examiner is requested to call Applicant's attorney at the telephone number shown below.

To the extent necessary, a petition for an extension of time under 37 C.F.R. 1.136 is hereby made. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to Deposit Account 500417 and please credit any excess fees to such deposit account.

Respectfully submitted,

McDERMOTT WILL & EMERY LLP



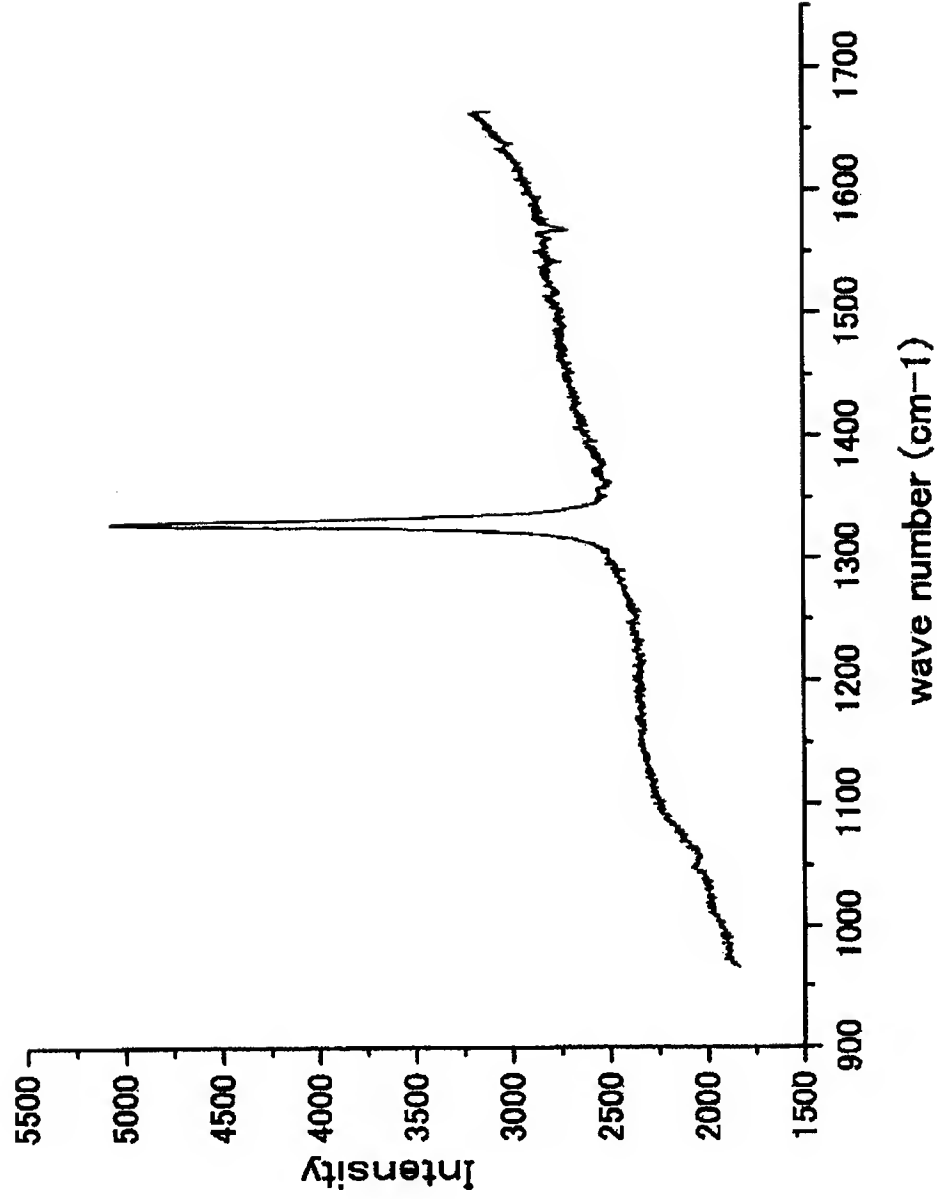
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Material (1)



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Raman spectral research on MPCVD diamond film

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Abstract Raman spectra of MPCVD diamond film have been studied. Based on the resonance size selection effect, we think that there is no nano-crystalline diamond in the sample and the Raman peak at 1145 cm^{-1} can not be considered as the characteristic peak of nano-crystalline diamond though it has been used as the characteristic peak of nano-crystalline diamond widely for many years.

Keywords: nano-crystal diamond, Raman spectroscopy, size confinement effect, size selection effect.

DOI: 10.1360/02ww0046

Diamond has many attractive physical properties such as ultra high hardness, high thermal conductivity and strength as well as low coefficient of friction and high electrical resistivity. However, the use of artificial diamond, even the micron-scale diamond film, is limited due to the intrinsic rough surface, low optical transparency and difficulties in further processing. Thus, the manufacture of nano-scale diamond film with smooth surface and high optical transparency has become the target of recent engineering efforts. Microwave plasma chemical vapor deposition (MPCVD) technology is considered to be a convenient and fast way to produce nano-crystalline diamond (NCD) film^[1].

The structure of newly made nano-scale materials needs to be verified and studied. This is important not only for fundamental research but also for practical application. Spectroscopy, especially, Raman spectroscopy has become one of the priority techniques because it can provide many crystalline information, as well as the structure and dynamics of elementary excitations. For example, the Raman peak at 1332 cm^{-1} is almost the only proof of crystalline diamond^[2]. However, the assignment of some characteristic peak is of suspect and has no solid scientific base^[3]. It has been thought that the Raman peak at 1145 cm^{-1} is shifted from the 1332 cm^{-1} peak due to the size confinement effect^[4], and thus has been used widely as the characteristic peak of NCD for many years. However, it is doubtful as the size confinement effect can not result in such a big shift of almost 200 cm^{-1} . Thus, it is critically needed for both research and application that the identification of characteristic peaks is based on the solid funda-

ment.

The size confinement effect is the one of basic effects of nano-scale systems. The phenomenon appeared in Raman spectrum due to this effect is that the Raman frequency shifts from the corresponding bulk frequency and the peak broadens with the size decrease of nano-scale systems. The samples produced by CVD method usually are the ones of a size distribution. For the size distributed nano-systems, when the excitation wavelength changes, the Raman frequency and peak width will shift and broaden, respectively, due to the difference of the resonance enhancement effect for different sizes of samples. This is known as the resonance size selection effect^[5]. Both effects mentioned above will result in a downshift of frequency with decreasing excitation wavelength for diamond samples.

In this paper, we will report on the identification of Raman peaks of a diamond film grown by MPCVD using different excitation wavelengths. Characteristic Raman peak of NCD is discussed emphatically at the same time.

1 Experiment result and discussion

The diamond film sample was grown on crystal silicon substrate by MPCVD. The atom force microscopy photograph of samples is shown in Fig. 1, showing that the grain sizes are not uniform. Renishaw 1000 Raman Microscope was used for all Raman spectral measurements. All Raman measurements were done at room temperature with back-scattering geometry. In addition to the scan mode, the static mode is also employed for more accurate frequency measurement. The measurements are performed at several points on the sample to eliminate any spurious data from inhomogeneity. No difference was observed at different sampling points. All the Raman parameters result from the fitting with Lorentzian line-shapes.

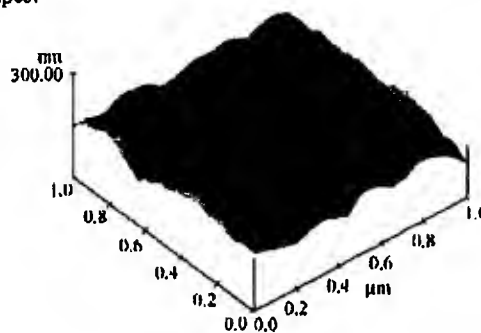


Fig. 1. AFM image of MPCVD diamond film sample.

Fig. 2 shows the Raman spectra of the diamond film sample at 515 and 325 nm laser. Fitted parameters of the Raman peaks are shown in Table 1. Five peaks can be distinguished at 1145 , 1333 , 1360 , 1480 , and 1560 cm^{-1} in Fig. 2. The 1333 cm^{-1} peak (labeled as #2) is the charac-

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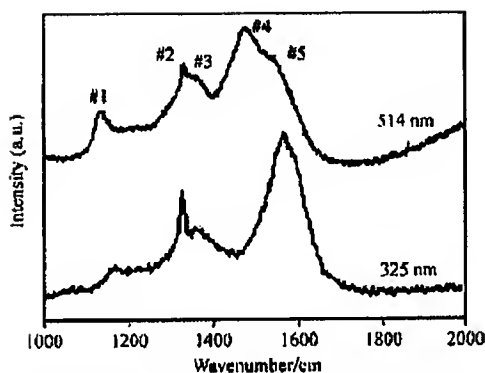


Fig. 2. Raman spectra of MPCVD diamond film sample excited by 515 and 325 nm lasers.

teristic peak of bulk diamond rising from sp^3 bond. The 1360 and 1560 cm^{-1} peaks (#3 and #5 peaks) are from sp^2 bonds and are commonly known as the D and G modes of graphite respectively^[2]. The 1480 cm^{-1} peak (#4 peak) is from the scattering of the diamond-like mode with sp^3 bond. The 1145 cm^{-1} peak (#1 peak) is the one that has been considered as the characteristic peak of NCD widely.

Table 1 Raman frequency (cm^{-1}) on excitation wavelength and its assignment for MPCVD diamond film sample

		#1	#2	#3	#4	#5
Excitation wavelength	515 nm	1145	1333	1360	1480	1558
	325 nm	1170	1333	1373	—	1578
Assignment		Diamond D mode		G mode	Diamond-like	

From Fig. 2 and Table 1, we can see that with decreasing excitation wavelength, the intensity of the #2 peak increases while the Raman frequency remains unchanged. This intensity variation agrees with the expectation that the Raman scattering intensity of sp^2 bond should enhance with increasing excitation energy^[6,7], while no frequency shift contradicts what predicted by the size selection effect. The above results indicate that the sample contains only the bulk diamond component but no nano-scale diamond. The intensity variation with the excitation wavelength for peak #5 follows the dependence sp^3 bond on the excitation wavelength. Finally, we note for peak #1 that the intensity becomes weaker remarkably and the frequency shifts from 1145 cm^{-1} to 1170 cm^{-1} as the excitation wavelength decreases. The above behavior is inconsistent with the intensity change induced by the diamond sp^3 bond and the varying trend due to the resonance size selection effect with the change of excitation wavelength, respectively. Thus the varying trend of intensities mentioned above indicates that peak #1 is not due to the scattering of diamond component. While the behavior of the

frequency change indicates that the sample is not the nano-scale diamond with a size distribution, which is intrinsic for CVD grown sample. Therefore we may conclude that the sample used here does not contain NCD and the appearance of the Raman peak at 1145 cm^{-1} is due to neither diamond nor nano-scale structure. In other words, the Raman peak at 1145 cm^{-1} cannot be considered as the characteristic peak of NCD.

The above conclusion may be confirmed by AFM image in Fig. 1, in which the grain size of sample is shown about 100–200 nm. This size is beyond the size range of so-called nano-materials. A more likely origin of this peak has recently been suggested by Ferrari et al.^[9]. They verified that the Raman peak at 1145 cm^{-1} is not from the scattering of NCD and is assigned to transpolyacetylene segments at grain boundaries and surfaces formed in the preparing.

2 Conclusion

In summary, based on the size confinement and size selection effects and with comparison of Raman spectra excited at different laser energies, we conclude that the diamond film sample grown by MPCVD is not the NCD sample even though it contains diamond component. Furthermore, we have found that the widely accepted characteristic Raman peak at 1145 cm^{-1} for NCD may not be correct. This work is not only giving a Raman peak identification of a practical sample but providing fundamental information that is important for the research of nano-scale materials.

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Origin of the 1150-cm⁻¹ Raman mode in nanocrystalline diamond

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The peak near 1150 cm⁻¹ in the visible Raman spectra of poor quality chemical-vapor-deposited diamond is often used as the signature of nanocrystalline diamond. We argue that this peak should not be assigned to nanocrystalline diamond or other *sp*³-bonded phases. Its wave number disperses with excitation energy, its intensity decreases with increasing excitation energy, and it is always accompanied by another peak near 1450 cm⁻¹, which acts similarly. This behavior is that expected for *sp*²-bonded configurations, with their smaller band gap. The peaks are assigned to transpolyacetylene segments at grain boundaries and surfaces.

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The chemical-vapor deposition (CVD) of diamond is an important route in the production of this unique material.^{1,2} Generally, the aim is to maximize the crystalline quality of CVD diamond. A single, sharp peak at 1332 cm⁻¹ in the Raman spectrum is frequently used as a signature of high crystalline quality.³ However, diamond grown under non-optimum conditions, such as lower temperature or higher carbon activity in the plasma, gives films with small grain size. This material is often called nanocrystalline diamond, even if the grain size is actually 5–100 nm. Recently, nanodiamond was grown intentionally under specific conditions,^{4,5} because smaller grains give films with valuable tribology and field-emission properties.⁶ The appearance of a 1150 cm⁻¹ Raman peak is very widely used as a simple signature of such nanocrystalline diamond. This paper argues that the 1150 cm⁻¹ Raman peak in fact cannot originate from a nanodiamond or related *sp*³-bonded phase, but must arise from a coexisting *sp*² phase, which we suggest is transpolyacetylene. Figure 1(b) shows a Raman spectrum of a typical low-quality CVD diamond, grown by microwave CVD at 1300-W, 780°C, 180-sccm H₂, 17.5 sccm CH₄, and 2.5 sccm CO₂ at 45 mbar.⁷ Similar spectra were seen by many groups (e.g., Refs. 1, 5, and 8–15). In addition to a small diamond peak at 1332 cm⁻¹, the spectrum has four extra features at 1150, 1350, 1450, and 1550 cm⁻¹. The peaks at 1350 and 1550 cm⁻¹ are the *D* and *G* modes of disordered carbon.³ The peak at 1150 cm⁻¹ has been attributed to nanocrystalline diamond.^{1,8} We refer to this peak as *v*₁, and to the 1450 cm⁻¹ peak as *v*₃.

Nemanich *et al.*⁸ proposed that the 1150 cm⁻¹ peak arises from nanocrystalline or amorphous diamond. A small grain size would be expected to relax the *q*=0 selection rule and allow phonon modes with *q*≠0 to contribute. Subsequent workers always supported this assignment.^{9–15} This is largely because this wave number corresponds roughly to a maximum in the vibrational density of states (VDOS) of diamond. We argue against this assignment for the following reasons. First, the idea that this peak is due to *q*≠0 phonons activated by disorder is ruled out because the grains are too large to observe a zone boundary peak at ~1150 cm⁻¹. Phonon confinement allows the participation of phonons with a wave vector *q*≈2π/*d*, where *d* is the grain size. Grains of 5–100 nm would still favor modes quite close to Γ , rather than modes nearer the zone boundary at *L*, which contribute most

to the VDOS maximum,¹⁶ seen in Fig. 1(c). Even if the grains were truly 1 nm or less, the VDOS maximum is near 1260 cm⁻¹, not 1150 cm⁻¹, so a single peak at 1150 cm⁻¹ would not be seen. The phonons in small grains could be softer than in bulk diamond. However, the Raman spectra of diamond nanocrystals from shock synthesis, with a fairly uniform distribution of grain sizes of 4–6 nm, were measured by Yoshikawa *et al.*¹⁷ and Obratsova *et al.*¹¹ They saw only the main diamond peak broadened and downshifted by ~12–13 cm⁻¹, consistent with phonon confinement,¹⁸ confirming that bulk-phonon dispersion curves are valid for nm-size grains.

Second, *sp*² sites have a much larger cross section for visible Raman than *sp*³ sites, about 50–230 times,¹⁹ but the intensity of *v*₁ is sometimes comparable to or even higher

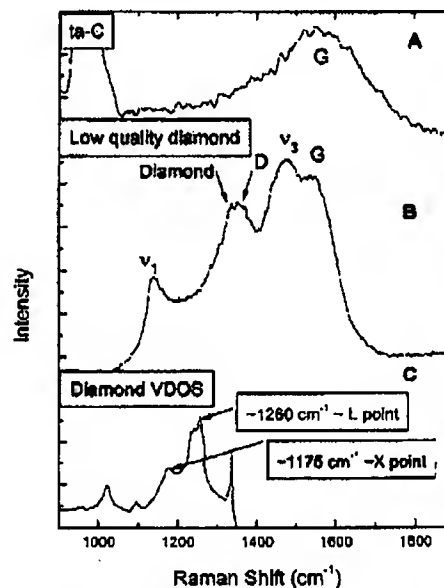


FIG. 1. Raman spectrum of (a) tetrahedral amorphous carbon and (b) a low quality CVD diamond at 514 nm. (c) The VDOS of diamond, from Ref. 16 for comparison; showing a maximum at 1260 cm⁻¹ and a kink at 1175 cm⁻¹. The peak at ~970 cm⁻¹ in (a) is due to Si second order.

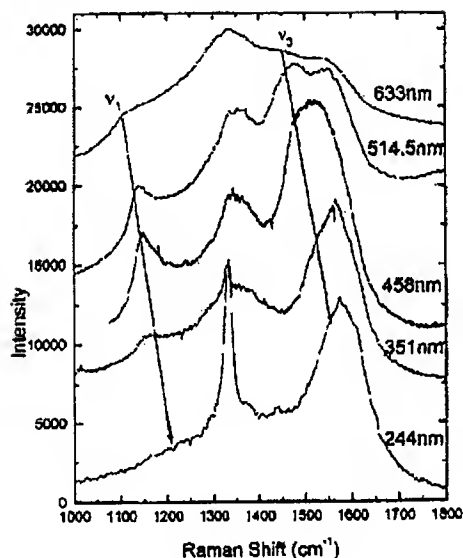


FIG. 2. Raman spectra of nanodiamond excited at different wavelengths. Unpolarized Raman spectra were acquired in back-scattering geometry. A Renishaw micro-Raman system modified for UV excitation was used to record spectra at 244 and 325 nm, from a frequency-doubled Ar-ion laser and a He-Cd laser. Another Renishaw system was used for 514.5 and 633 nm spectra from Ar-ion and He-Ne lasers. A Dilor XY system was used for spectra at 351 and 458 nm from an Ar-ion laser.

than the amorphous carbon phase and crystalline diamond phase [Fig. 1(b)]. If the nanocrystalline diamond is located in rather wide grain boundaries, for example, where is the much larger signal from the sp^2 graphitic sites, which are also in the grain boundaries? In low-quality diamond, one expects the Raman signal from sp^2 sites to dominate that from sp^3 sites.

The third and fourth reasons are the key ones, and can be understood from Fig. 2. This shows Raman spectra taken at various laser excitation energies on a region of suboptimal CVD diamond film. We see that the ν_1 and ν_3 peaks in fact disperse by 50–100 cm^{-1} with excitation energy. This is not possible for a density-of-states feature, which should remain fixed as the excitation energy varies. Fourth, the intensity of the ν_1 and ν_3 peaks decreases compared to the 1332 cm^{-1} diamond peak, as the excitation energy is raised. If the two modes were both due to sp^3 sites, they would both increase in intensity as the excitation energy is raised. This is because sp^3 sites have a wide, 5.5 eV band gap. Raising the excitation energy allows the sp^3 bonds to be excited more strongly. In contrast, sp^2 sites have a low band gap and are easily excited by visible light. We see that the 1150 cm^{-1} mode is in fact absent at 244 nm excitation, where sp^3 sites have their highest cross section. A decrease in intensity of the 1150 cm^{-1} mode compared to the 1332 cm^{-1} mode suggests that the 1150 cm^{-1} mode is due to sp^2 sites of some type.

It has been suggested that the 1150 cm^{-1} mode may be

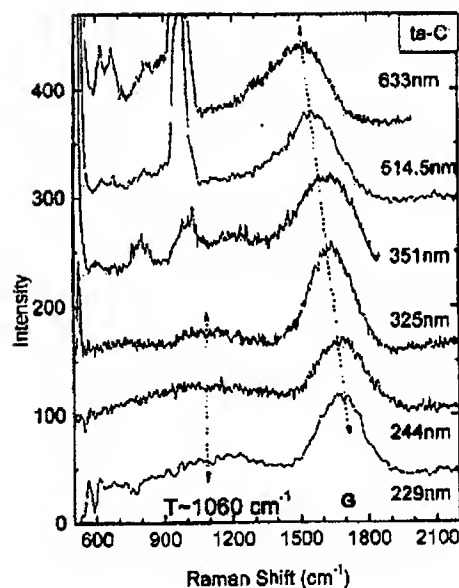


FIG. 3. Raman spectra of *ta-C* as a function of excitation wavelength. The *T* peak at $\sim 1050 \text{ cm}^{-1}$ seen for UV excitation is labeled. The low-frequency peaks for visible excitation are the first and second orders of the Si substrate (Ref. 27); note the combination modes of Si between 600 and 700 cm^{-1} (Ref. 27), which are clearly seen at 633 nm, due to the low absorption of the sample at this wavelength. The peak at $\sim 800 \text{ cm}^{-1}$, seen at 351 nm excitation wavelength, is a spurious peak due to the optics of the 351 nm Raman system.

caused by hexagonal diamond.^{8,10} However, it is now known³ that hexagonal diamond has a Raman mode at 1323 cm^{-1} , just below that of cubic diamond.

A further reason is that the 1150 cm^{-1} mode usually has a companion mode around 1450 cm^{-1} . This is seen in Fig. 2, but it is sometimes obscured by the tail of the *G* peak of the disordered carbon phase at 1560 cm^{-1} . It has been suggested that the 1450 cm^{-1} mode could be due to SiC in the films.⁸ This can be ruled out, as it is still seen in diamond on non-silicon substrates.¹³ It has also been attributed to some form of sp^3 bonding.^{8,11,14,15} This can be ruled out because sp^3 bonding can only give modes up to about 1350 cm^{-1} , the band limit of diamond.¹⁶

The final argument against assigning the 1150 cm^{-1} peak in the visible Raman spectrum to sp^2 sites, is the Raman spectrum of tetrahedral amorphous carbon (*ta-C*). This is an amorphous carbon with about 85–90% sp^3 bonding. Figure 3 shows its Raman spectra for increasing excitation energy. It is seen that at visible excitation (e.g., 514 nm), the spectra is dominated by a very broad *G* peak at around 1560 cm^{-1} (Ref. 20); see Fig. 1(a). There is no mode near 1150 cm^{-1} . The spectra change with increasing excitation energy. Only at deep UV excitation, 244 nm or 5.1 eV, does the spectrum have a broad peak centered on 1050 cm^{-1} . This is a VDOS feature of the random sp^3 network.²¹ The high excitation energy allows sp^3 sites to be excited with a cross section

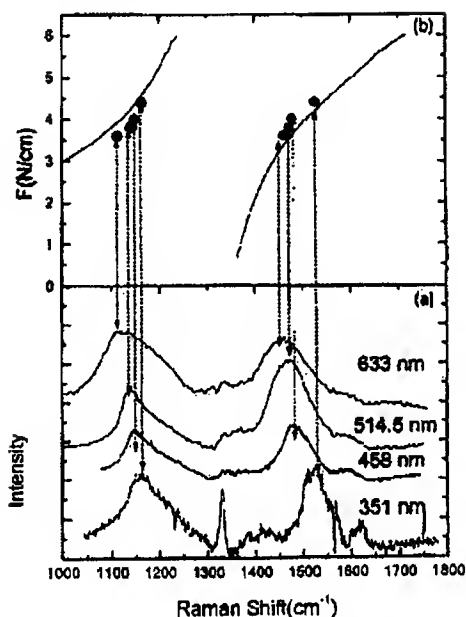


FIG. 4. (a) Raman spectra of Fig. 2 after removal of G and D peaks near 1550 and 1350 cm^{-1} of the α -C phase. This leaves the zone-center mode at 1332 cm^{-1} (nondispersive) and two new modes at ~ 1150 and 1450 cm^{-1} labeled ν_1 and ν_3 . (b) Comparison of the ν_1 and ν_3 modes to the theoretical dispersion relation for transpolyacetylene (Refs. 22 and 23).

comparable to sp^2 sites. However, this 1050 cm^{-1} peak is not present for visible or near-UV excitation. The 1050 cm^{-1} peak only appears in UV excitation, so its intensity has the opposite dependence with excitation to ν_1 , so these peaks cannot be related.

The spectra of Fig. 2 were fitted with four Lorentzians, with all parameters free. We then subtracted the D and G peaks to give the residual intensity, shown in Fig. 4(a). This clearly shows the dispersion of these peaks. We assign the 1150- and 1450 cm^{-1} peaks to the ν_1 and ν_3 modes of transpolyacetylene (trans-PA) (explaining our terminology).^{22,23} These modes are roughly sum and difference combinations of $\text{C}=\text{C}$ chain stretching and CH wagging modes. Trans-PA is an alternate chain of sp^2 carbon atoms, with a single hydrogen bonded to each C. The possibility of trans-PA in CVD diamond has been suggested previously from a surface-enhanced Raman scattering (SERS) study.²⁴

The dispersion of the ν_1 and ν_3 modes arises naturally in this model. The dispersion arises because the conjugated π bonding along the PA chain is broken into segments of different conjugation lengths. The local band gap of each segment increases as the length decreases. Varying the excitation energy selectively tunes into a segment with that length and excites it. The vibrational frequency of the segments also varies with the conjugation length, so the mode wave number increases as the segment length decreases. The conjugation length can be represented by an average force constant

F . F is smaller for longer conjugation lengths. Figure 4(b) plots the calculated ν_1 and ν_3 against F for trans-PA itself.^{22,23} The observed positions of the ν_1 and ν_3 peaks in our low-quality diamond are seen to lie close to these reference lines. The observed ν_1 and ν_3 follow the same trend as the reference curves, which confirms our assignment of these two peaks. The F vs ν plot also allows one to derive the effective conjugation length of the trans-PA chains. We find a length of 6–15 $\text{C}=\text{C}$ units, as the excitation changes from 325 to 633 nm.

In a previous SERS study of trans-PA in CVD diamond, the sample showed only the 1332 cm^{-1} diamond peak in normal Raman.²⁴ SERS also enhanced a small peak at ~ 1240 cm^{-1} , which was attributed to nanocrystalline diamond, due to its negligible dispersion.²⁴ Although its position agrees with the maximum in the diamond VDOS, we disagree with this assignment. Indeed, this peak is further evidence of trans-PA as trans-PA normally has a third peak ν_2 at this frequency,^{22,23} with smaller intensity than ν_1 and ν_3 , and a very small dispersion with excitation energy.^{22,23} We did not observe ν_2 in our spectra, due to its small intensity and the dominance of the D peak at that frequency.

The ν_1 and ν_3 modes of trans-PA are clearly connected to the presence of hydrogen. Indeed, a post-deposition anneal of low-quality CVD diamond causes the ν_1 and ν_3 modes to disappear,¹¹ which is consistent with the loss of hydrogen. The need for hydrogen also accounts for why the ν_1 and ν_3 modes are not seen in nanocrystalline diamonds prepared by shock synthesis. The Raman spectra of such diamonds shows a broadening and lowering of the 1332 cm^{-1} mode, expected from phonon confinement, but not of the 1150 cm^{-1} mode.^{11,17}

Finally, we note that fitting broad visible Raman spectra of amorphous carbons with a set of Gaussians can sometimes give a peak around 1150 cm^{-1} .^{25,26} This should not be taken as evidence of sp^3 bonding, but that a multi-Gaussian fit may be inappropriate.

In summary, the suggestion that peaks near 1150 and 1450 cm^{-1} in the Raman spectra of low quality CVD diamond are due to nanocrystalline or amorphous diamond is critically examined. It is found not to be possible to link these peaks to $\text{C}-\text{C}$ sp^3 vibrations. The peaks are assigned to transpolyacetylene lying in grain boundaries. The origin of such polyacetylene must be related to the deposition mechanism. The amount of polyacetylene is probably very small, as it has a large Raman cross section.²⁷

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